

# COATINGS. ENAMELS

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## LOW-MELTING COATINGS FOR GLASS DECORATION

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The optimum titanium-bearing lead-free glass compositions have been developed for producing low-melting white coatings on sheet glass. The properties of glasses and coatings and their structure and phase composition are studied. The optimum conditions for the formation of coatings are determined.

Decorating articles with low-melting coatings, transparent or opaque (enamels), makes it possible to enhance their artistic value, improve their external appearance, and expand the range of products. The glass compositions and the methods for coating formation are selected based on the service conditions and the shape and size of articles to be decorated with low-melting coatings.

The compositions most commonly used in production of coatings are lead-containing glasses possessing all the necessary parameters: a low melting temperature, good spreadability, luster, and color purity. However, their toxicity calls for the development of new lead-free low-melting glass and enamel compositions [1–3].

The purpose of the present study was to develop lead-free compositions for opaque low-melting decorative coatings and to investigate the conditions of their formation.

The system chosen for the study was  $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{TiO}_2 - \text{P}_2\text{O}_5 - \text{RO} - \text{R}_2\text{O}$ , which is the most promising with respect to its low-melting properties [4].

As the coatings have to satisfy a number of requirements, the following chemical compositions were developed (wt.%): 23–41  $\text{SiO}_2$ , 17–26  $\text{B}_2\text{O}_3$ , 1–3  $\text{Al}_2\text{O}_3$ , 1–5  $\text{P}_2\text{O}_5$ , 8–14  $\text{TiO}_2$ , 0–17  $\text{ZnO}$ , 0–3  $\text{CaO}$ , 10–20  $\text{Na}_2\text{O}$ , 0–18  $\text{K}_2\text{O}$ , and 0–5  $\text{Li}_2\text{O}$  (Ukrainian patent No. 11007) [5].

The batch was prepared of the traditional raw materials: quartz sand, boric acid, soda, potash, lithium carbonate, sodium polyphosphate, chalk, and zinc, aluminum, and titanium oxides.

The glasses were melted in a muffle electric furnace in corundum crucibles of 0.1–0.5-liter capacity. The maximum glass-melting temperature was 1050–1300°C with 1-h exposure. The samples were molded by casting glass melt on a metal plate and in molds. To obtain a granulated material,

the glass melt was poured in water with subsequent drying. Glass powder was obtained by milling the granulated glass in a ball mill.

The properties of glasses and coatings were studied using the standard methods [6]. The TCLE within the temperature interval 20–400°C was measured with a DKV-5AM dilatometer with an accuracy of  $\pm 1 \times 10^{-7} \text{ K}^{-1}$ . The water resistance was determined using the granular method with a precision of  $\pm 0.1 \text{ cm}^3/\text{g}$ . The capacity of glass for coating formation was determined in a gradient furnace by applying powder on a sheet glass. The relative evaluation of the water resistance of a coating was obtained by determining its hydrophoby (wettability). The resistance of the coating to the effect of alkaline solutions was determined in boiling samples in 2%  $\text{Na}_2\text{CO}_3$  solution for 3 h, and the resistance to acid solutions was determined by holding the samples at room temperature for 1 h in 0.25% acetic acid solution. The extent of the coating spread was determined according to GOST 24405–80 on tableted samples compressed from the glass powder.

The properties of the developed glasses and coatings are shown in Table 1.

It is established that the TCLE of most coatings lies within the range close to the TCLE of sheet glass:  $(90 - 108) \times 10^{-7} \text{ K}^{-1}$ , and the dilatometric temperature of the beginning of softening does not exceed 570°C. The synthesized glasses according to their water resistance belong to hydrolytic classes III–IV.

The processes occurring in glass fusion and coating formation were studied using differential thermal analysis. The general character of transformations in the glasses considered is shown in Fig. 1. The DTA curves of glasses 4 and 6 exhibit a clear endothermic effect with a minimum at 610°C and exothermic effects in the temperature range 670–760°C.

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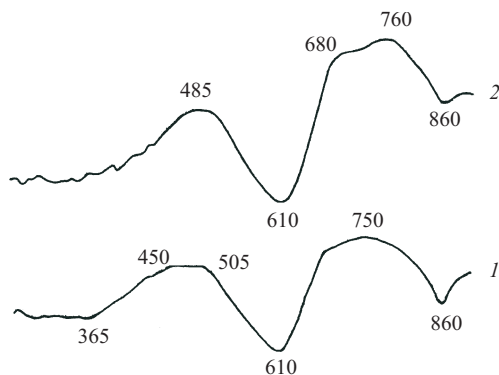


Fig. 1. Thermograms of glass 4 (1) and 6 (2).

The exothermic-effect maximums at 680°C are rather intense, which is evidence of the high crystallization capacity of the glasses. The significant similarity of the endothermic and exothermic effects suggests that crystallization proceeds under a high viscosity of glass, and the blurred exothermic effects at 750–760°C indicate either the crystallization of two phases or recrystallization of one of them [7]. The endothermic effects in glass 6, which are better defined than those in glass 4, point to a higher crystallizing capacity of glass 6, where crystallization occurs not just on the surface but in the bulk as well. The maximum endothermic effect corresponding to 860°C is presumably determined by the melting of crystalline phases.

The crystalline phases arising in thermal treatment of glasses 4 and 6 were identified with a DRON-2 x-ray diffractometer and a Tesla 30305 scanning microscope. Diffraction patterns were taken of the coatings deposited on a sheet glass substrate.

The diffraction patterns of coatings 4 and 6 (Fig. 2) exhibit the diffraction maximums typical of the following titanium dioxide modifications: rutile ( $d/n = 0.324, 0.248, 0.218$  nm), anatase ( $d/n = 0.351, 0.244, 0.190$  nm), and partly brookite ( $d/n = 0.347, 0.290, 0.248, 0.188$  nm) [8]. In

addition to these, low-intensity reflections of aluminum and potassium titanate are registered. The intensity of the diffraction maximums in coating 4 is lower, which points to a lesser degree of crystallization, and their blurred shape is evidence of a substantial quantity of the vitreous phase. Anatase prevails in the diffraction pattern of coating 6, which determines the whiteness of this coating. Thus, in the case of titanium-bearing glasses one can speak of the formation of sodium titanate at the first stage, and then rutile  $\alpha$ -TiO<sub>2</sub> is formed on its basis. Later on, anatase  $\beta$ -TiO<sub>2</sub> is formed independently.

The microphotos of the coatings suggest that coating 4 has a heterogeneous structure and contains a great quantity of the vitreous phase, in which crystalline inclusions are distributed (Fig. 2a and b). According to the data in [8], these needle-shaped crystals belong to rutile. Coating 6 has a more uniform crystalline microstructure: apart from the fine-crystalline rutile, it has large pyramidal and prismatic crystals, which are identified as anatase [8], whereas the vitreous phase is expressed to a lesser extent (Fig. 2c and d).

Accordingly, the structure of developed titanium-containing coatings is a heterogeneous system with a chaotic distribution of crystals of different shapes and sizes and vitreous interlayers.

The slip or the paste for coatings was prepared by thorough mixing of the synthesized glass powder with a binder and solvents. In order to apply a coating using the screen printing method, a paste was prepared based on AS 5114 binding mixture, which contains acrylic resin and Tetralin, as well as binding mixtures based on water-soluble products from the Clorvinil company (Kaluga, Russia). The optimum ratio between the glass powder and the binding mixture in the paste is equal to (1.25–1.30) : 1.0. In spray deposition of coatings, a slip consisting of a binding mixture based on carbomethyl cellulose and the glass powder was used. The working viscosity of the slip determined on a VPZh-2 capillary viscometer amounted to 17–20 sec.

TABLE 1

Glass	Melting temperature, °C	Color		TCLE, $10^{-7} \text{ K}^{-1}$	Dilatometric softening temperature, °C	Water resistance of glass		Coating formation temperature, °C	Spread extent, mm	Chemical resistance of coating		
		of glass	of coating			cm <sup>3</sup> /g	hydrolytic class			weight loss, mg/dm <sup>2</sup>		wetting angle, deg
										in 2% Na <sub>2</sub> CO <sub>3</sub>	in 0.25% CH <sub>3</sub> COOH	
1	1200	Gray-white	White	120	540	0.9	IV	600 – 620	40	121	9	60.5
2	1250	The same	The same	112	540	0.6	III	620 – 640	30	57	11	59.5
3	1250	"	"	104	565	0.5	III	590 – 600	35	63	16	57.5
4	1100	Light gray	"	108	570	0.8	III	600 – 620	25	101	14	58.0
5	1100	The same	"	90	570	1.4	IV	580 – 600	40	82	17	60.0
6	1100	"	"	98	525	1.8	IV	590 – 610	47	49	5	62.5
7	1300	Grayish-yellow	"	102	540	0.8	III	560 – 590	48	38	8	61.0
8	1300	The same	"	98	560	0.7	III	580 – 600	46	67	14	60.5
9	1200	Brown	Brown	101	570	1.6	IV	580 – 600	42	33	12	62.0
10	1200	Green	Sky-blue	97	530	2.0	IV	580 – 600	43	85	16	61.5

The decorative coatings were formed in a muffle electric furnace and at the factory production lines for horizontal and vertical hardening of sheet glass. The main parameters determining conditions for the coating formation are the heat-treatment temperature and duration. It is established that the minimum heat-treatment duration for the formation of high-quality coating at the 600–650°C is 5–8 min.

All coatings based on glasses 1–8 (Table 1) were opacified and had a white color. The coating based on glass 9 containing 2% manganese oxide (above 100%) was brown, and the coating based on glass 10 containing 3% copper oxide (above 100%) was sky-blue.

The spread extent of the developed coatings satisfies the requirements imposed on industrial coatings.

The studies of the chemical resistance of the obtained coatings indicated that their resistance to acid and alkaline media is satisfactory. The water wettability of the coatings was estimated based on a contact wetting angle equal to 57.5–62.5°, which is evidence of their sufficient water resistance.

Based on the studies performed, an optimum lead-free glass composition was selected to be used to produce low-melting white coatings (wt.%): 35–37 SiO<sub>2</sub>, 21–26 B<sub>2</sub>O<sub>3</sub>, 1–2 Al<sub>2</sub>O<sub>3</sub>, 3–5 P<sub>2</sub>O<sub>5</sub>, 10–12 TiO<sub>2</sub>, 1–3 CaO, 10–15 Na<sub>2</sub>O, 3–6 K<sub>2</sub>O, and 0–3 Li<sub>2</sub>O. Using inorganic pigments (Mn<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>), brown coatings of different tints were synthesized for sheet glass decoration.

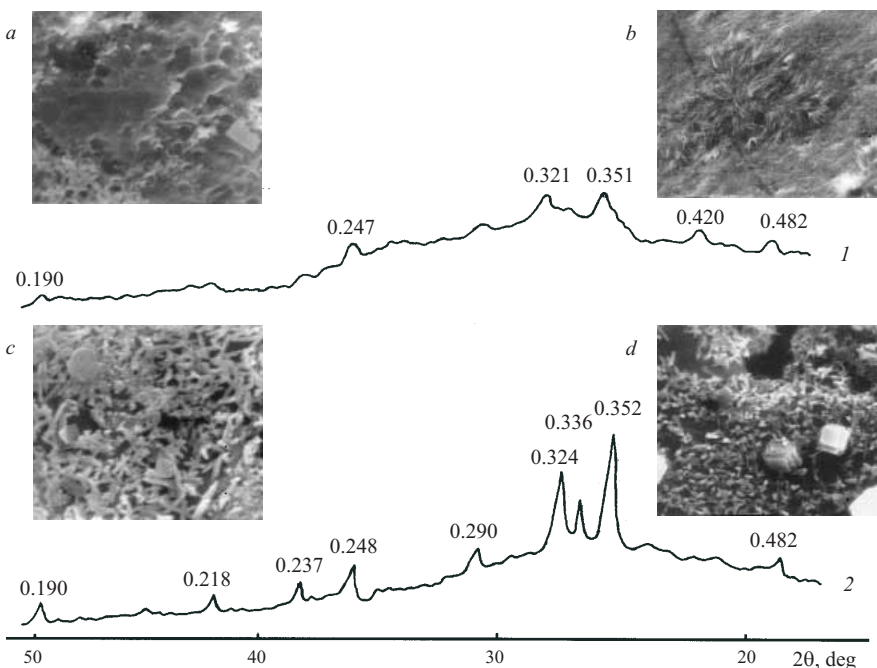
The studies performed on the production lines for hardening sheet glass demonstrated that high-quality coatings can be produced on the basis of glasses 6, 7, and 9. They are distinguished by their clarity of lines, purity of color, luster, and good spreadability and adhesion to glass and do not form chips and cracks. The formation of the coatings proceeded under the following conditions:

– on a glass-hardening line in a horizontal furnace: temperature  $t_1 = 720 - 840^\circ\text{C}$ , process duration  $\tau_1 = 2 \text{ min } 15 \text{ sec}$ ,  $t_2 = 720 - 800^\circ\text{C}$ ,  $\tau_2 = 3 \text{ min } 20 \text{ sec}$ ;

– on a glass-hardening line in a vertical furnace:  $t_1 = 740^\circ\text{C}$ ,  $\tau_1 = 3 \text{ min } 40 \text{ sec}$ ;  $t_2 = 760^\circ\text{C}$ ,  $\tau_2 = 4 \text{ min } 10 \text{ sec}$ .

It should be noted that the best-quality coatings are produced when the heat treatment lasts at least 4 min.

Thus, based on the studies performed, the optimum compositions of titanium-bearing lead-free glass were determined for producing low-melting coatings on sheet glass.



**Fig. 2.** Diffraction patterns and microphotos of coatings made of glasses 4 (1) and 6 (2): a, b ( $\times 15,000$ ) glass 4; c ( $\times 15,000$ ), d ( $\times 10,000$ ) glass 6.

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